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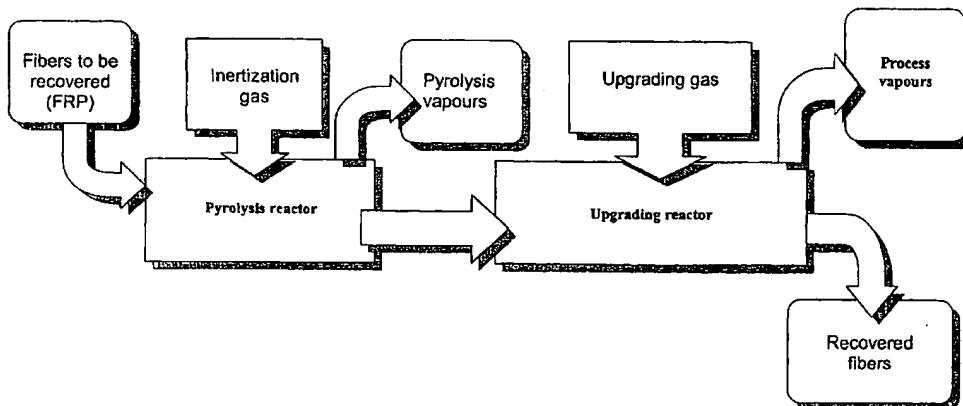
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(54) Title: METHOD AND APPARATUS FOR RECOVERING CARBON AND/OR GLASS FIBERS FROM A COMPOSITE MATERIAL



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(57) Abstract: The present invention relates to a method aimed at recovering carbon and/or glass fibers, by means of pyrolysis and subsequent upgrading treatment, from scraps and processing waste of composite material of fibers with FRP (Fiber Reinforced Plastics) plastic materials coming from different stages of industrial processing and from manufactures at end of life. The method provides the pyrolysis of scraps, waste and composite materials of FRP to eliminate the plastic matrix and a subsequent hot treatment, in presence of upgrading gas, of the recovered fibers for removing carbon residues. The fibers recovered from the treated manufactures can be reutilized in the manufacturing of products with mechanical features very similar to the ones of the rolled sections produced with virgin fibers. The cost of CF (carbon fibers), recovered with the proposed method, has been calculated to be equal to 20-30% of the one of the new carbon fibers.



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## METHOD AND APPARATUS FOR RECOVERING CARBON AND/OR GLASS FIBERS FROM A COMPOSITE MATERIAL

The present invention substantially relates to a method aimed at recovering carbon and/or glass fibers from composite materials in polymeric matrix (also known as FRP: Fiber Reinforced Plastics), coming from 5 different industrial processing stages and/or from manufactures at end of life, by means of a pyrolysis thermal treatment and of a subsequent cleaning treatment from residues, the latter being called "upgrading".

10 The involved commodity field is that of the production of second raw materials derived from industrial waste with particular attention to the mechanical die.

15 Carbon, glass, etc. fibers are the material which is wanted to be recovered from the scraps and from the industrial production waste, with a combined process of pyrolysis and subsequent upgrading of the fibers.

20 Currently, CFRP scraps and waste are sent to dump and they represent a cost both for the firms producing the waste and for the community. In fact carbon fibers, or CF, are not recovered from CFRP.

25 The analysis of the state of art has pointed out that the results obtained with other recovery methods have not achieved conditions so as to justify the industrial use thereof due to problems connected to the quality of the obtained products, to the cost of the

processes or to the industrial applicability of the processes themselves.

One of the main problems met in the recycle processes of carbon fibers (CF) is the separation thereof from resins or from the plastic matrix in general. In fact, the separation process usually results to be uneconomical.

Up to now, the dissolution of resin in chemical solvents has been the most advantageous technique experimented for this purpose. However, the solvent containing the dissolved resin creates serious risks for the environment especially if the solvent quantity used for this process is high.

Furthermore, this process does not allow recovering carbon fibers from the composite materials which have already undergone the whole processing, that is the reticulation process and resin cure up to the end product.

The recovery of the reinforcing fibers of the composite materials according to the invention allows to industrially reutilize, pursuant to European Community and national rules, a more and more huge waste flow, which otherwise would be destined to be confined into dump.

By way of information, in table 1 the consumptions in Europe of carbon fibers or CF are listed.

Table 1

Consumptions of carbon fibers in Europe ( Source: AKZO NOBEL FIBERS S.r.l.)				
	1995	1996	1997	1998
Consumption ton/year	1700	2000	2200	2700

Currently the production of carbon fibers is represented by 95% by the "3000 high-toughness filament" type, the selling price thereof fluctuates between 51.50 and 77.50 Euro/kg, according to 5 quantities.

CF physical-mechanical features are considerably better than the ones of the materials used nowadays (nylon, glass fibers, etc.) to produce fabrics and tapes of unidirectional fibers.

10 In fact carbon fibers have a tensile strength ten times greater than high-resistant steels and also the other mechanical features such as compressive strength, flexural strength, torsional strength, etc. are considerably higher than the other materials for 15 mechanical constructions. The rolled sections produced with CF are among the most advanced manufacts used in modern technologies. The density of these new materials is less than a half of light alloys and it is about five times smaller than steels, even if at the same 20 time it provides a much higher resistance. It is then evident that practically all construction materials can be replaced by composite materials, when hardness superficial features and/or a particular resistance to high temperatures are not required, to great advantage 25 to the considerable decrease in weight, the mechanical features of the manufact being the same.

Nevertheless, the CF high market price strongly limits the use thereof in conventional uses.

The increase in the CFRP utilization in 30 aeronautical, automotive, nautical, etc. industry determines a considerable increase in production waste

and scraps, which currently have as end destination the dump disposal with considerable additional costs for the industry.

To exactly understand the extent of the CR utilization in this field, it has to be noted that the quantity of carbon fibers used to construct an aeroplane varies from 13 to 20% of the aircraft weight: this quantity is constantly increasing.

The more and more considerable use of CF has further determined, during the years, a set of obsolete means destined to scrapping, which, in turn, cause disposal problems.

It is therefore the main object of the present invention to provide a method for recovering carbon fibers from composite materials reinforced with resins, also called CFRP, aimed at reutilizing the same in the production of manufacts having mechanical features very similar to the manufacts produced with "virgin" carbon fibers.

This has been achieved, according to the present invention, by providing a method wherein the composite materials therefrom the reinforcing fibérs have to be recovered, undergo a heat treatment which sets carbon and/or glass fibers free from the resinous matrix and allows the recovery and the reutilization thereof for all the conventional applications wherein "virgin" carbon or glass fibers are used. The treatment steps are a pyrolysis of the material to decompose the resinous matrix and an "upgrading" step of the recovered fibers, wherein the recycled fibers are cleaned from the carbon residues of the first step in

order to allow the reutilization thereof to produce new composite materials.

It is also an object of the present invention a plant for carrying out said process.

5 A better understanding of the invention will occur with the following detailed description and by referring to the figures which illustrate, by way of example and not for limitative purposes, a preferred embodiment for the carbon fibers.

10 In the drawings:

Figures 1, 2 and 3 show the starting materials utilized to feed the plant performing the treatment thereof according to the method sofar described;

15 figures 4 and 5 respectively show stereomicroscope and optical microscope photos of fibers impregnated with epoxy resin;

figures 7 and 8 respectively show optical microscope photo and SEM image of the solid residue after the pyrolysis treatment;

20 figure 9 shows the microanalysis performed on the fibers of figures 7 and 8;

figures 10 and 11 show the SEM image of the reinforcing fibers recovered after the upgrading step;

25 figure 12 is a block diagram underlining the main steps of the developed process, either in continuous (or flow) and in batch; and

figure 13 is a block diagram of the implemented plant.

30 The process according to the invention substantially comprises two subsequent steps, pirolysis and upgrading, which take place preferably in

consecutive way inside a reactor: the material pyrolysis to decompose the resinous matrix by setting free the fibers and the upgrading to clean the recycled fibers from carbon residues of the preceding step.

5       The upgrading is performed by supplying a reactive gas flow to the reactor: the main upgrading gases are CO<sub>2</sub>, air, oxygen, vapour; they can be used on their own or mixed, even with other gases.

10      It has to be noted that the distinction between the two steps, pyrolysis and upgrading, is purely formal, since the same can take place without interruption: for example, by utilizing air as process gas, it is obtained that, during heating of the composite material, the fibers undergo the upgrading 15 while the process advances. In other words, pyrolysis and upgrading take place at the same time, since whereas some fibers undergo pyrolysis, some others are subjected to upgrading and this without interrupting the process nor adding reaction gas.

20      Advantageously, the method can be extended to any other kind of composite material formed by fibers in polymeric matrixes.

25      As it will seen better hereinafter, the process conditions of the first and of the second step (process temperature, gas flow, residence time, upgrading gas) vary with the starting material.

The recovered fibers can be used for preparing manufactures, by utilizing them as such (sheets or fiber fragments) or after trimming the same.

30      It is to be noted that the pyrolysis process, which itself has been a well known process for many

years, has never been applied in significant way to scraps and CFRP waste for the recovery of carbon fibers. According to the invention, to make possible this application it has been necessary to set up the 5 geometrical parameters and the management mode of the plant as well as the parameters conditioning the kinetics of the process itself.

The pyrolysis, which as already said is the first step of the method which is described (figure 12), 10 consists in the thermal degradation process performed in absence of oxygen, by means of indirect heating. The material supplied to the reactor undergoes a thermal cracking, by resolving into one solid and one volatile component.

15 The volatile fraction can undergo cooling and partial condensation by producing one liquid fraction and one incondensable gaseous fraction.

The application of the pyrolysis process to CFRP leads to the following products:

- 20 - gaseous fraction, mainly constituted by hydrogen, methane, ethylene, ethane and carbon oxydes;
- oily fraction, constituted by organic substances condensable at room temperature and pressure;
- solid fraction, constituted by the recovered carbon 25 fibers coated with the residue coming from the resin cracking.

Percentages and compositions of the above-mentioned fractions depend upon conditions thereunder the process is performed and mainly upon:

- 30 - temperature of the material in the pyrolysis reactor;

- working pressure;
- contact time;
- presence or not of catalysts.

Table 2 shows the commodity composition typical  
 5 for CFRPs; tables 3 and 4 respectively show the immediate and average elementary analysis for CFRPs,  
 whereas figure 6 shows the qualitative microanalysis of the resin present on starting fibers: it is to be noted  
 the presence of O, S and Cl in the resin. The presence  
 10 of Au is determined by the metalization of the sample.

Tab. 2 – CFRP commodity analysis.

CFRP components	Chemical composition	weight %
Carbon fibers	Carbon	54
Resin	C,H,N,S,O, ecc. <sup>(a)(b)</sup>	36
Antiadherent film	C, H *	10

- 15 (a) percentages are calculated by comprising metals, catalysts and cross-linking agents added in the preparation processes of resins and films;  
 (b) sometimes in the resins small quantities of Cl and Br (about 0.5%) may be present due to the resin precursors (es. epichlorohydrin for epoxy resins) or to antiknock compounds.

Tab. 3 – CFRP immediate analysis.

Humidity(%)	Volatiles (%)	Fixed carbon (%)	Ashes (%)
0,07	32,28	66,45	1,2

Tab. 4 - Average elementary analysis for CFRP

Element	Percentage
C	80,8
H	2,7
N	6,5
S	1,5
O (by difference) <sup>(a)</sup>	7,3
Ashes	1,2

(c) it is to be noted that the organic O percentage is calculated by difference and therefore it comprises possible existing halogens.

5 During the first step of the process the material supplied to the plant is treated then at temperatures ranging from 250 to 700°C and with a residence time of a few hours.

10 The residence time depends upon the reactor geometry, upon the O<sub>2</sub> percentage and upon the temperature. It is important to underline that, from the implementation point of view, the pyrolysis reactor and the upgrading reactor can coincide, that is they can be constituted by the same reactor wherein both 15 steps occur.

The process environment is guaranteed either by pyrolysis gases developing in the reactor or by a nitrogen flow, utilized as conveying gas of the produced vapours.

20 The weight percentages of the products obtained by pyrolysis of CFRP composite materials at a process temperature of 550°C are the following, on the average:

- 60÷70% solid residue, containing recovered carbon fibers, deposited carbon, inert feedstocks and 25 metals;
- 10÷30% oily fraction;
- 10÷20% gas.

Gas, mainly constituted by light hydrocarbons, has a lower calorific power equal (or net heat value) to 30 about 8,000 kcal/Nm<sup>3</sup>. It can be utilized as fuel and it helps heating the pyrolysis reactor so as to amortize process costs.

The oily residue, which has a calorific power around 10,000 Kcal/kg, is constituted by aromatic, aliphatic components and by olefines; even such fraction can be utilized to supply energy to the process.

For the objects here described, the preferred solution consists in utilizing the pyrolysis vapours as such, without condensation, to supply energy to the process.

The solid residue is constituted by recovered carbon fibers and by charcoal which will be removed during the upgrading procedure of fibers.

The content in ashes is almost exclusively constituted by inert feedstocks and by metals, added as catalysts utilized during the manufacturing processes of the composite materials.

It has to be noted that the weight percentage of the solid fraction differs by about 10% from the quantity of fibers existing in the original composite material, as shown by data of the commodity analysis: this 10% represents the carbon residue generated by the thermal cracking of the resin (the decomposition of the polyethylene film does not produce appreciable quantities of solid residue).

Figures 7 and 8 show the solid residue after the pyrolysis treatment: the fibers are coated with a layer of material. The performed microanalysis, shown in figure 9, has pointed out that this material is very rich in carbon and it has appreciable quantities of O, S and Cl.

The material is surely a char due to cracking of

the resin, wherein O, S and Cl were previously present.

The presence of carbon residue on fibers causes a great change in their properties, by making them hard, stiff and fragile and then it prevents the reuse  
5 thereof.

Impregnation tests of fibers with epoxy resins to obtain again the starting manufacts have demonstrated that apart from influencing the processability of fibers, the carbon residue strongly limits the adhesion  
10 of fiber with the resin, causing to obtain inferior manufacts.

The second part of the process performs indeed the "improvement" (upgrading) of recovered fibers, by implementing the removal of the carbon residue.

15 The upgrading step is consecutive to the pyrolysis step and it preferably takes place without any operation of cooling, opening and discharging of the reactor. The upgrading process could also be made either in parallel to the pyrolysis analysis or  
20 subsequently, otherwise with a combined pyrolysis/upgrading process in a single step.

The upgrading is carried out by supplying to the reactor a flow of reactive gas (such as for example CO<sub>2</sub>, air, oxygen, vapour and mixtures of the same  
25 gases) so as to remove from fibers the carbon deposits without damaging the fibers themselves.

The process temperature, the gas flow and the residence time (which shows contact time of fibers with gas at the process temperature) vary according to the  
30 utilized process gas.

For example, by using air in mixture with nitrogen

in 30:70 proportion (O<sub>2</sub> percentage in the gaseous flow equal to 6%) at a temperature of 500÷700°C with a residence time of gas in the reactor equal to about ten minutes, the residence time for the upgrading on the 5 average results to be 2÷3 hours.

Figures 10 and 11 show the SEM image of recovered CF: as it can be seen, fibers are clean and well distinct one from the other.

Table 5 shows the results of the elementary 10 analysis performed on recovered CF.

Tables 6 and 7 respectively show the results of traction tests performed on virgin carbon fibers and on the ones recovered under different process conditions and the properties percentage loss.

15

Tab. 5 - Elementary analysis on recovered CF

Element	Percentage
C	92,01
H	0,10
N	6,65
S	0
Ashes	1,2

20

Tab. 6 – Mechanical tests on recovered fibers: calculation of σ(N/mm<sup>2</sup>)

breaking load

Sample	Fiber length (mm)		
	1=50	1=25	1=10
White	3302,3	3651,2	4556,8
A500	2873	3435,3	4065,8
A550	2711,6	2928,6	3519,1
A600	2428,2	2818	3223,6

Tab. 7 – % loss in breaking load of fiber samples with respect to WHITE

Sample	Fiber length (mm)			Average value
	l=50	l=25	l=10	
A500	13.0	5.9	10.8	9.9
A550	17.9	19.8	22.8	20.2
A600	26.5	22.8	29.3	26.2

The recovered fibers can be used for preparing manufacts, by using them as such (sheets or fiber fragments) or after trimming the same.

5 In the first case, fibers are used in the original form of fabric, by re-impregnating them with resin and by processing them, or by crumbling them and producing a casual scattering of the same on a resin layer, the MAT (non-woven fabric), which can be then processed.

10 Obviously, the procedure and preparation conditions vary according to the type of resin, or plastic material, used for preparing composite materials.

15 Hereinafter, by way of example, the description of a method used for preparing rolled sections based upon recovered carbon fibers with an epoxy resin is shown.

20 The manufacts have been prepared starting from sheets or fragments of carbon fibers, as obtained after recovery and cleaning treatment; samples have been obtained by means of impregnation in epoxy resin and subsequent polymerization and cure.

25 A relative composition of fibers and resin of about 3/2 has been used (60% of weight by fibers, 40% of weight by resin): such composition has been calculated starting from the densities of components and it allows obtaining an end manufact with a density in fiber volume equal to about 50%.

The preparation can be schematized as follows:

A) Preparation of matrix

The matrix has been prepared by making epoxy resin to react in stoichiometric quantities with the cross-linking agent (72% resin, 18% cross-linking agent), at room temperature and until obtaining a homogeneous product.

B) Preparation of preimpregnated

Weighed quantities of matrix have been spread on subsequent sheets of crossed fibers, so as to obtain a 4-layer rolled section, 100x100 mm in size. The manufact, coated with an antiadherent film, has been firstly inserted into vacuum stove, at a pressure of 0.1 atm (to allow removing volatile substances from the reaction environment) and then cold subjected to the pressure of some atmospheres, to uniformly impregnate the fibers with resin and to discharge therefrom the exceeding quantity. The so-obtained preimpregnated material has been kept into refrigerator to prevent resin reticulation.

C) Cure and post-cure of the manufact

The sample, set free from the antiadherent film, has been placed between two steel mirror plates and subjected to the cure thermal treatment, carried out under press, at the temperature of 70°C for 2 hours, at the pressure of 6÷8 atm. The preparation has ended with the post-cure treatment, performed in stove at the temperature of 140°C for 2 hours.

By referring to the block diagram of figure 13 the implemented plant provides the following main sections:

- 1) reaction section, wherein the pyrolysis and

upgrading steps take place in sequence;

- 2) fume-treating section, optional for the process, wherein the pyrolysis and upgrading vapours are treated in order to allow the discharge into atmosphere of cleaned gases, as well as the cogeneration.

The fume-treating section may comprise:

- a "quenching" subsection (optional), for separating the condensable fraction from the pyrolysis vapours;
- a "scrubbing" subsection (optional), for washing the process gases from the acid components (e.g. HCl, H<sub>2</sub>S, etc.);
- an oxidation subsection, wherein the process gases undergo the complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O and which provides the energy for the process;
- a discharge subsection wherein the combustion fumes are cleaned and then discharged by a chimney.

By using then the guidelines previously shown, summarized in figure 13, the process can be applied indifferently in plants implemented for operating in batch or flow.

The process for the recovery of fibers according to the present invention has been experimented by using a "CRFP" pilot plant designed and manufactured to develop the treatment.

Figure 14 is a simplified process diagram of the implemented plant.

The main procedures of the processing are:

- 1) Reactor loading;
- 2) material pyrolysis;
- 3) upgrading;

4) cooling and discharge.

In this case, as there has been already a chance to mention, the two steps take place in sequence in the same reactor.

5       The statement that the distinction between the two steps is to be considered purely formal, is confirmed by the fact that they can take place also without an evident separation; for example, it is possible to provide a "flow" plant wherein a fluid bed exploiting  
10      air as process gas is utilized as reactor: in such case, fibers will be supplied from the bottom in the same direction of gas. Therefore, it is possible to implement a heating gradient from the bottom upwards, so that in the low area of the reactor the first  
15      pyrolysis step takes place (in this case temperature is low and air does not react); as the gas gradually transports fibers in areas with higher temperature, the upgrading reaction begins to be thermodynamically promoted, which then, upon leaving the reactor,  
20      completes the fiber recovery process.

Another possible solution, wherein different areas of a same reactor are used to make the "flow" process to occur, is to utilize a conveyor belt for transportation, or a "drop-in" system of the material,  
25      always in the same direction of the process gas, but in opposite direction to the heater vector, so as to implement the conditions mentioned above.

However, the flow process can be implemented by simply following the diagram of figure 12 and by  
30      utilizing for the pyrolysis and upgrading steps two rotating-drum reactors, in series one to the other, or

any other technology usually utilized to carry out thermotreating processes.

Advantageously, it is also possible to utilize the same plant as described in figure 14 to carry out the 5 "flow" process, by implementing other two reactors which utilize the same section of treating vapours and fumes; in this case the three reactors will be operated alternatively, so that when the reactor 1 is in the process step, the reactor 2 is in the loading and 10 heating step and the reactor 3 is in the cooling and discharging step.

At this point, it is interesting to examine in more details the conditions of the upgrading step.

What follows refers to the upgrading step of 15 fibers performed under ideal conditions (in laboratory, by neglecting problems due to scattering or reactor geometry) by utilizing oxygen as upgrading gas.

The used oxygen is that of the air, enriched during some tests (as it will be seen later) with 20 technical oxygen.

Although hereinafter carbon fibers are referred to, the same considerations can be extended to glass, kevlar, etc. fibers.

Table A1 shows the dependence of cleaning time 25 upon process temperature by utilizing air as upgrading gas.

Table A1

Sample	Cleaning time (min.)	Temperature (°C)
1	60	500
2	20	550
3	10	600
4	2	700

Other tests have been performed under the same conditions as above highlighted, by utilizing a flow of air enriched with oxygen to increase the quantity of reactive agent, the flows being the same.

Table A2 relates to the dependance of cleaning time upon process temperature by utilizing air enriched with oxygen ( $O_2$  end content 45%) as upgrading gas.

10

Table A2

Sample	Cleaning time (min.)	Temperature (°C)
5	180	400
6	90	450
7	20	500

Table A3 shows the dependance of cleaning time upon the  $O_2$  percentage present in the gaseous flow at the temperature of 500°C.

Table A3

Sample	Cleaning time (min.)	% O <sub>2</sub>
8	60	20
9	50	25
10	40	30
11	25	37
12	20	45

15

By examining the features of the treated fibers, it has been noted that an increase in the oxygen percentage in the gaseous flow, even if it leads to a decrease in the cleaning time, attacks fibers in an excessive way, by determining the weakening thereof in

some places.

Therefore, the use of air (not enriched) guarantees a more controlled, even if slower, reaction.

Based upon the data shown in tables A1+A3 it has  
5 been chosen to utilize an operating temperature of  
about 500÷600°C in air, to be experimented then on  
pilot scale.

However, it is to be underlined that data refer to  
ideal conditions, that is experiments carried out in  
.10 single layer and on small samples (absence of  
scattering phenomena due to the sample mass and to the  
reactor geometry).

What has been said can be extended to upgrading  
processes which use different reactive gases such as  
15 CO<sub>2</sub>, steam and others, used on their own or in mixture,  
able to remove the residual charcoal from the pyrolysis  
process of fibers by reaction.

It has to be highlighted that the optimum process  
conditions (process temperature, residence time, speed  
20 of gaseous flow, etc.) vary with the used gas and the  
type and quantity of treated material. For example, it  
is known that the conversion reaction of coal with CO<sub>2</sub>  
is much slower than the one with oxygen and it takes  
place in significant way from 800°C upwards.

25 A process utilizing carbon dioxide as upgrading  
gas has the drawback of longer residence time of the  
material in contact with gas, higher temperatures  
(therefore higher energy consumption), but it involves  
a more controlled attack of the reagent (less  
30 aggressive) and then less damage to fibers.

Similar remarks can be made for steam or gas

mixtures.

The use of the method sofar described involves several advantages:

- possibility of recovering carbon and glass fibers  
5 from composite materials of the same reinforced with epoxy resins (FRP), coming from scraps and waste produced in different industrial processing steps and from manufacts at end of life; the recovered fibers can be reutilized in the production of  
10 manufacts with mechanical features very similar to the ones produced with "virgin" carbon fibers;
- potential economic saving due to missed conferring to dump of scraps and waste produced in different industrial processing steps and from manufacts at  
15 end of life;
- availability of a "source" of carbon, glass, etc. fibers, to manufacture composite materials, also in countries where the production of such fibers does not exist;
- 20 - possibility of obtaining carbon fibers with considerable reduced costs and with mechanical properties similar to "virgin" fibers;
- the lower cost of recovered fibers compared to "virgin" fibers makes possible the use thereof for  
25 new applications, up to now not considered for the high price of the "new" material.
- the recovered fibers can be reutilized as such in the manufacturing process of new composite materials or they can be trimmed and reutilized to produce MAT  
30 (unwoven fabric), by utilizing fibers distributed randomly on a layer or to produce felts.

The present invention has been described and illustrated in a preferred embodiment thereof, but it is clear that any person skilled in the art could apply modifications and/or replacements equivalent from the 5 technical and/or operating point of view, however comprised within the protective scope of the present industrial invention.

CLAIMS

1. Method for recovering reinforcing fibers from composite materials of the same in polymeric matrixes (also known as FRP: Fiber Reinforced Plastics), coming 5 from different industrial processing stages and/or from manufactures at end of life, characterized in that the composite materials therefrom the reinforcing fibers have to be recovered undergo a thermal treatment in two steps apt to set free the reinforcing fibers (for 10 example of carbon and/or glass) from the plastic matrix by allowing the recovery and reuse thereof for all the conventional applications wherein "virgin" reinforcing fibers are utilized; said two steps of the treatment respectively being a pyrolysis of the material apt to 15 decompose the plastic matrix by setting free the fibers, followed by an "upgrading" step of the recovering fibers, wherein the recycled fibers are cleaned from carbon residue of the pyrolysis step in order to allow the reuse thereof for manufacturing new 20 composite materials.

2. Method according to claim 1, characterized in that said two subsequent steps, pyrolysis and upgrading, take place in consecutive way inside a reactor.

25 3. Method according to the preceding claim, characterized in that the upgrading step is performed by supplying to the reactor a flow of reactive gas suitable to react with the carbon residue of pyrolysis, such as for example carbon dioxide, air, oxygen, 30 vapour, which are utilized on their own or in mixture in any percentage, also with other gases.

4. Method according to anyone of the preceding claims, characterized in that the pyrolysis step is performed by thermally degrading the composite material to be treated in absence of oxygen, so that the 5 material supplied to the reactor undergo a thermal cracking, by resolving into one solid and one volatile component.

5. Method according to anyone of the preceding claims, characterized in that during the pyrolysis 10 step the material is treated at temperatures ranging between 250-750°C and with a residence time of some hours, depending upon the typology of the material to be treated, the geometry of the reactor, the temperature, and all other process conditions.

15 6. Method according to anyone of the preceding claims, characterized in that the process environment is guaranteed either by the same pyrolysis gases developing into the reactor and by the use of a flow of an inertization gas, utilized also as conveying gas of 20 the produced vapours.

7. Method according to the preceding claim, characterized in that the process vapours are utilized as fuel and contribute to heat the reactor so as to amortize process costs.

25 8. Method according to claim 2, characterized in that the upgrading step preferably occurs without any cooling, opening and discharge procedure of the reactor.

9. Method according to anyone of the preceding 30 claims, characterized in that the treated materials are scraps and processing waste and manufacts at end of

life of FRP and they are processed without any pretreatment.

10. Method according to the preceding claims,  
characterized in that the recovered fibers are reused  
5 as such in the manufacturing process of new composite  
materials, or they are trimmed and utilized to produce  
MAT (non-woven fabric), by utilizing fibers distributed  
randomly on a layer or to produce felts.

11. Plant for the recovery of reinforcing fibers  
10 from the composite materials of the same in polymeric  
matrixes (also known as FRP: Fiber Reinforced  
Plastics), coming from different industrial processing  
stages and/or manufacts at end of life, characterized  
in that it comprises a reaction section, wherein the  
15 pyrolysis and upgrading steps take place in sequence.

12. Plant according to the preceding claim,  
characterized in that it further comprises a fume-  
treating section, wherein the pyrolysis and upgrading  
vapours are treated to allow discharging the cleaned  
20 gases into air, as well as the cogeneration.

13. Plant according to claim 11 or 12,  
characterized in that it comprises:  
a) an oxidation subsection, wherein the process gases  
undergo the complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O and  
25 which provides the energy for the process;  
b) a discharge subsection wherein the combustion fumes  
are cleaned and then discharged by a chimney.

14. Plant according to the preceding claim,  
characterized in that it further comprises:  
30 - a "quenching" subsection, for separating the  
condensable fraction from the pyrolysis vapours;

- a "scrubbing" subsection for washing the process gases from the acid components (such as for example HCl, H<sub>2</sub>S, etc.).

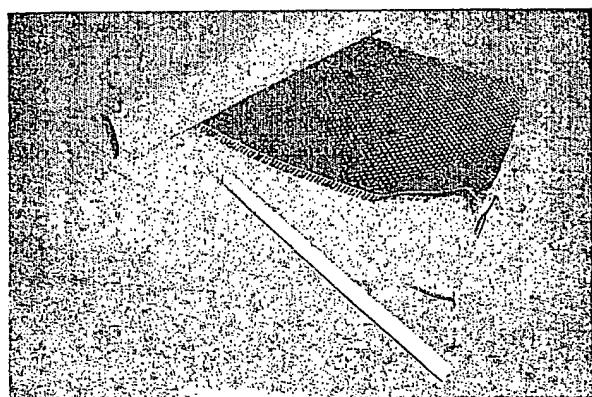


FIG. 1

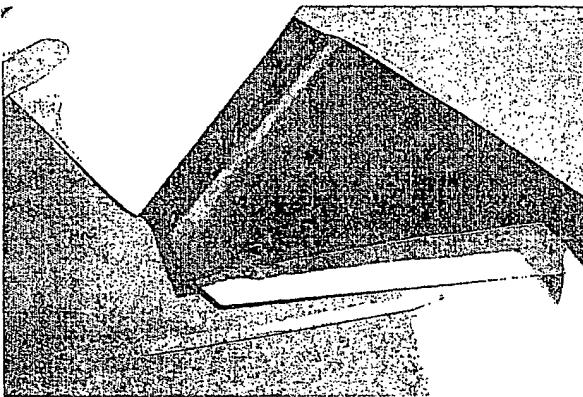


FIG. 2

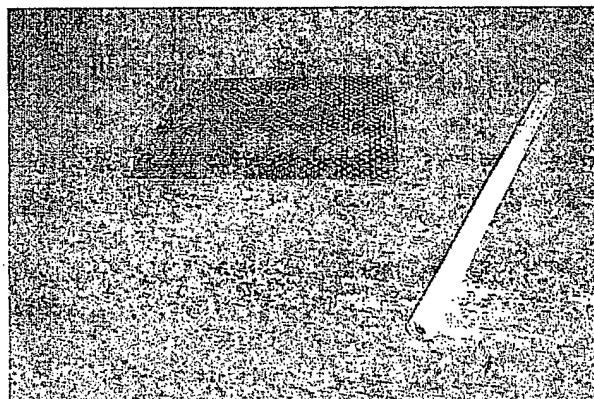


FIG. 3

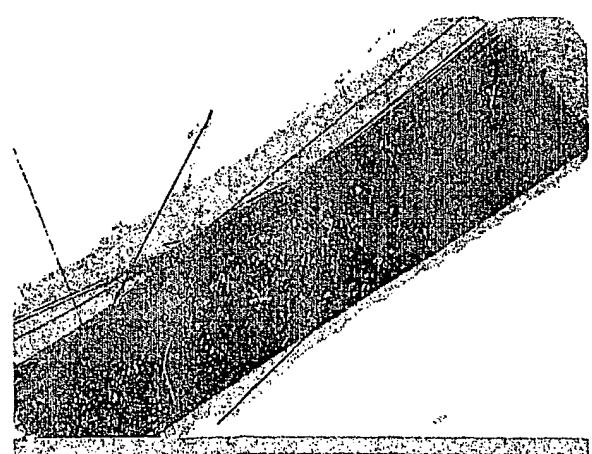


FIG. 4

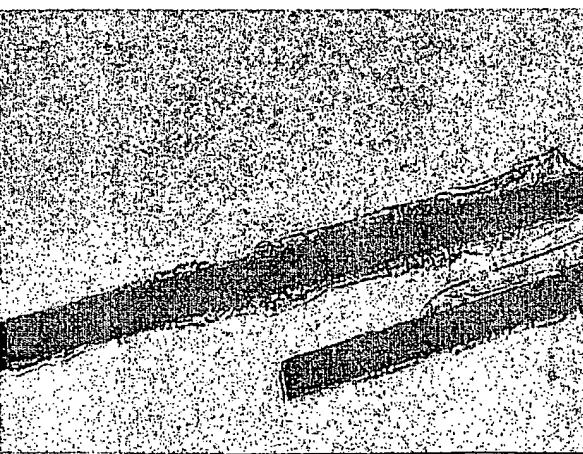


FIG. 5

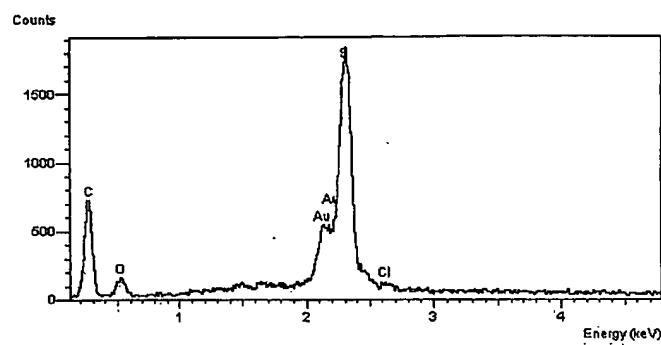


FIG. 6

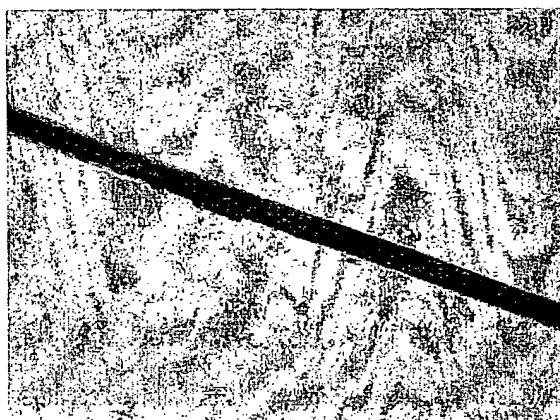


FIG. 7

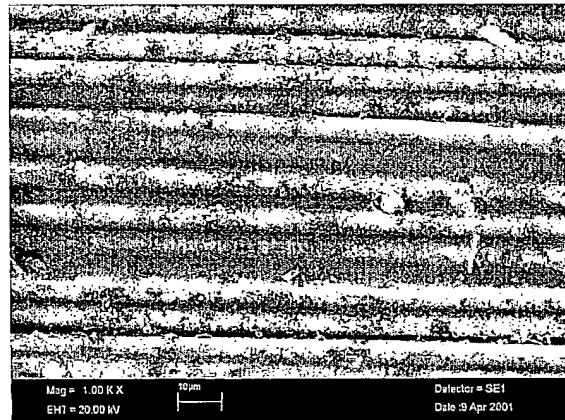


FIG. 8

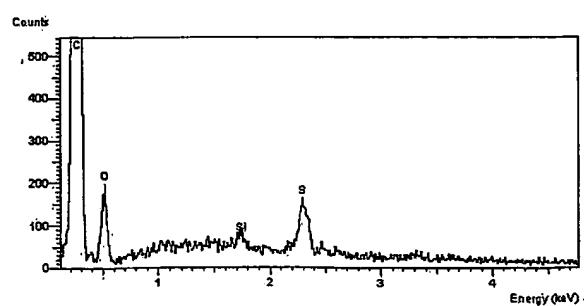


FIG. 9

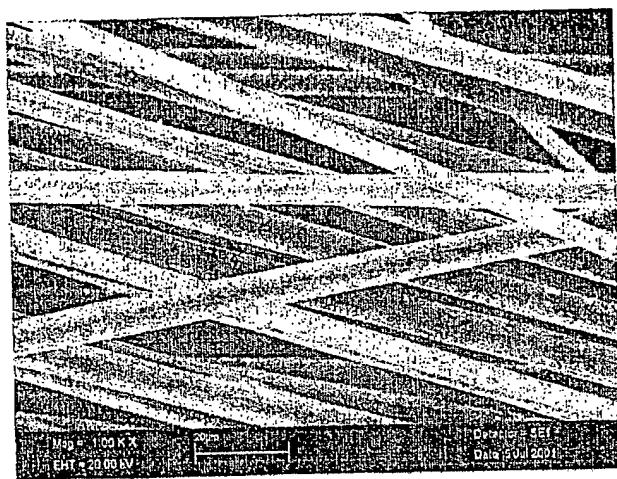


FIG. 10

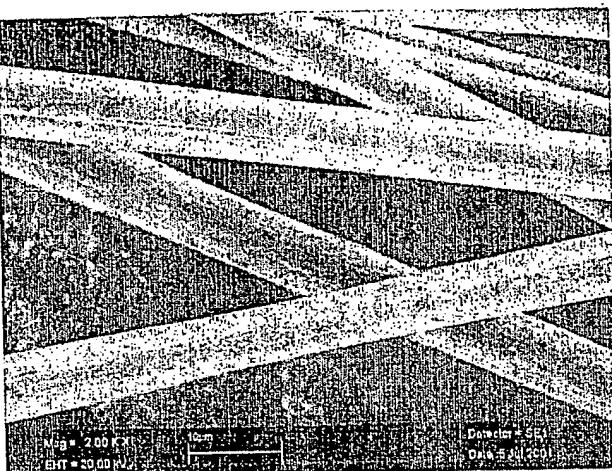


FIG. 11

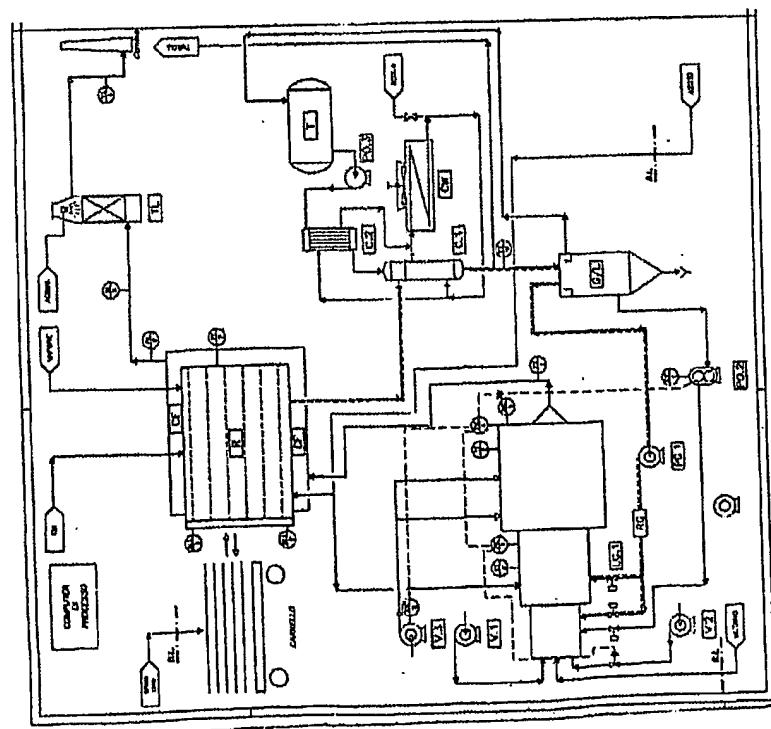


FIG. 14

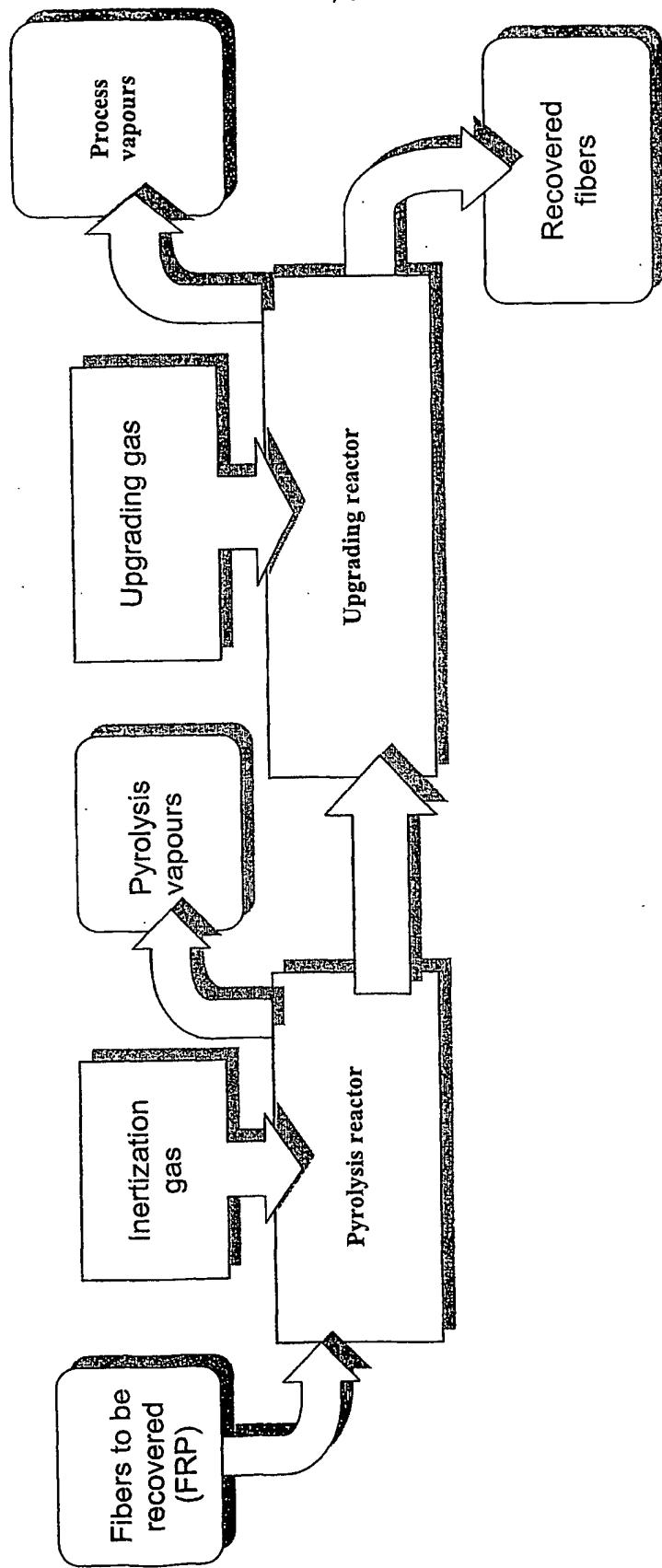


FIG. 12

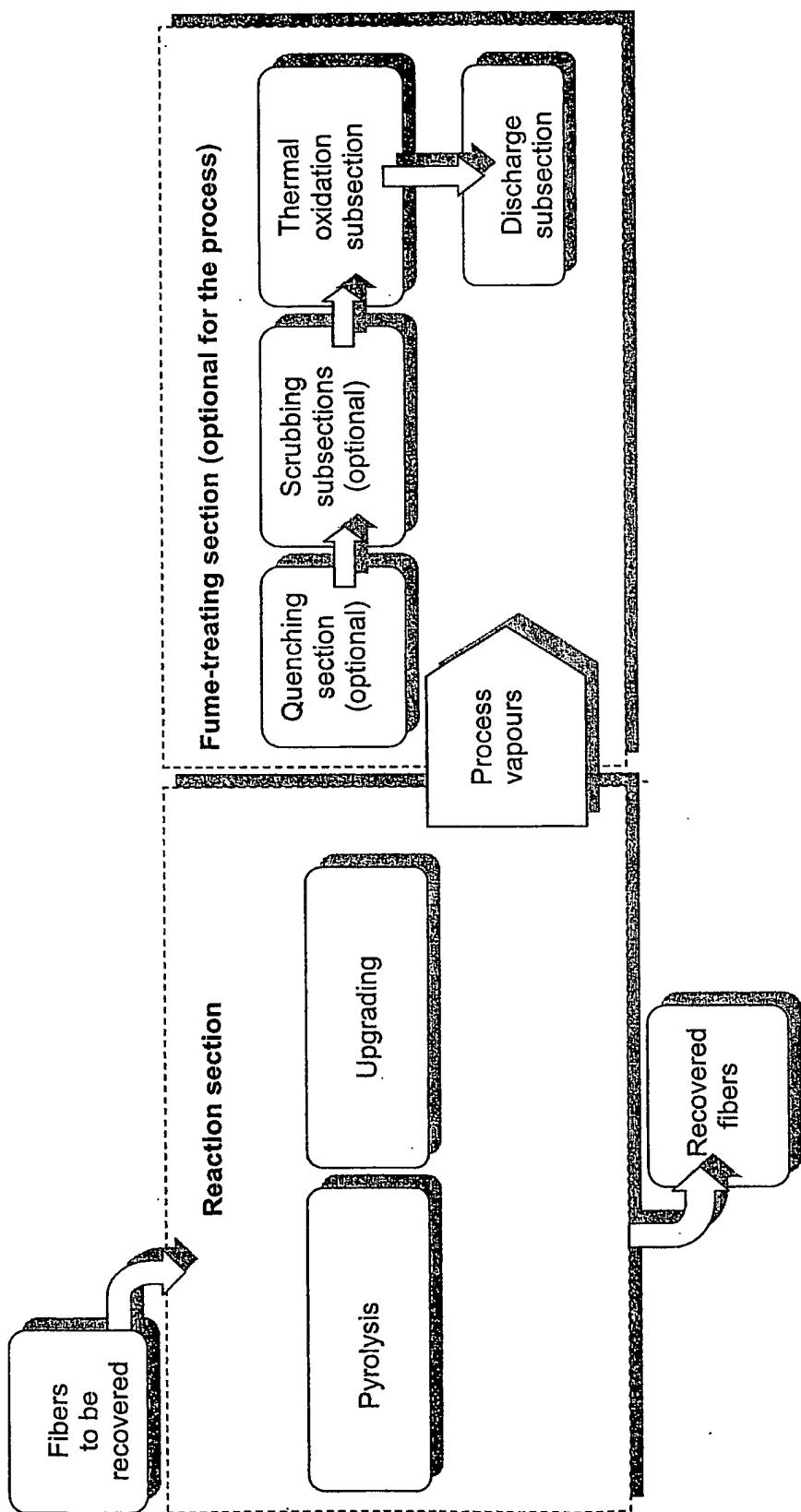


FIG. 13

## INTERNATIONAL SEARCH REPORT

PCT/IT 03/00247

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 B29B17/02 C08J11/12 C10B53/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29B C08J C10B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 198 018 A (AGARWAL KEDAR B) 30 March 1993 (1993-03-30) column 1-2 column 3, line 12-19 column 4, line 41 column 9, line 16-30 ----	1-14
X	US 4 647 443 A (APFFEL FRED) 3 March 1987 (1987-03-03) the whole document ----	1-14
X	EP 0 360 171 A (BUDD CO) 28 March 1990 (1990-03-28) page 4, line 29-36; figure 1 page 5, line 11-15 ----	1-14
	-/-	

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Date of the actual completion of the International search

13 August 2003

Date of mailing of the International search report

22/08/2003

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A	US 4 412 889 A (OECK ROBERT C) 1 November 1983 (1983-11-01) abstract ---	1-14
A	JP 52 084261 A (KOGYO GIJUTSUIN) 13 July 1977 (1977-07-13) abstract; figure 1 -----	1-14

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